

# PATENT SPECIFICATION

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## (54) PHOTOPOLYMERISABLE COMPOSITIONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photopolymerisable compositions comprising one or more materials, which may be monomeric or polymeric, which can be polymerised or cured by treatment with acids. Such materials are commonly referred to, and are referred to herein, as acid-polymerisable or acid-curable materials and examples of suitable materials are epoxide monomers, episulphide monomers, polyepoxides or epoxy resins, polyepisulphides or episulphide resins, phenol/formaldehyde resins, melamine/formaldehyde resins, urea/formaldehyde resins, cyclic ethers and thio-ethers (other than epoxides and episulphides) and polymers thereof, lactones, styrene, vinyl ethers and thio-ethers and resins which contain a cross-linking agent to cross-link or cure the resin when treated with acid. The invention relates in particular to compositions comprising one or more acid-polymerisable or acid-curable materials and at least one photosensitiser which initiates polymerisation or curing of the composition when the composition is exposed to radiation of suitable wavelength.

It is well known that acid-curable resins such as phenol resins and amino resins can be cured by irradiation with ultra-violet, actinic or electromagnetic radiation in the presence of a compound which generates an acid (which term includes Lewis acids) when exposed to ultraviolet radiation. Examples of compounds which have been proposed for use in such compositions are halogen-containing compounds, for example bromoform, carbon tetrabromide, hexabromoethane, 2,5 - dimethyl - tribromoacetophenone, 2,2,2 - trichloro - 4' - tertiarybutyl acetophenone, halomethylated benzophenones,  $\alpha$ -methylol benzoin sulphonic acid esters and aryl diazonium salts of metal halogenides.

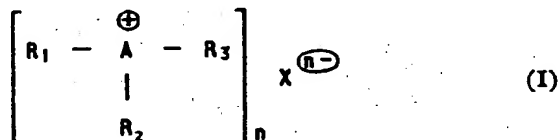
It is also well known that epoxy resins can be cured by irradiation in the presence of a substance which generates a Lewis acid when exposed to suitable radiation. Substances which have been proposed for use in epoxy materials include transition metal carbonyls and  $\alpha,\beta$ -unsaturated nitrosamines as well as  $\alpha$ -methylol benzoin sulphonic acid esters and aryl diazonium salts of metal halogenides mentioned above. The aryl diazonium salts of metal halogenides have also been proposed for polymerisation of epoxide monomers.

The photosensitive substances proposed hitherto for incorporation in acid-polymerisable or acid-curable materials are activated to release an acid upon exposure to ultra-violet or electromagnetic radiation or actinic radiation comprising a high proportion of ultra-violet radiation. However, the compositions proposed hitherto have not proved satisfactory. Transition metal carbonyls are toxic and slow acting and their use is undesirable. Generally, N-nitrosamines are carcinogenic and slow acting. Use of aryl diazonium salts of metal halogenides results in compositions which polymerise rapidly and which are subject to premature gelation and cannot be stored satisfactorily for any length of time even in the dark. It has been proposed to incorporate stabilisers or gelation inhibitors into epoxy materials containing aryl diazonium salts of metal halogenides in order to inhibit premature gelation of the

compositions and confer storage ability in the dark; this increases the cost of the compositions and moreover does not yield entirely satisfactory results even under carefully controlled storage conditions. Moreover the aryl diazonium salts generate nitrogen gas when the composition is irradiated and the resulting cured material may contain undesirable gas bubbles.

We have now found that incorporation of some salts of sulphur, selenium or tellurium into acid-polymerisable and/or acid-curable materials provides photopolymerisable compositions which overcome the disadvantages of the compositions proposed hitherto. Thus, for example, compositions containing the photosensitisers can be stored for prolonged periods in the dark without noticeable gelation occurring and the need to provide gelation inhibitors is obviated.

According to the present invention, there is provided a photopolymerisable composition comprising at least one acid-polymerisable or acid-curable material and as photosensitiser at least one salt of formula



wherein A is sulphur, selenium or tellurium, n is 1 or 2, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, which may be the same or different, each is a hydrocarbon or substituted hydrocarbon group or heterocyclic group or two of the groups R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> together with the element A are a heterocyclic structure, the other group R being a hydrocarbon or a substituted hydrocarbon group, and X<sup>n-</sup> is an anion derived from an acid which is capable of polymerising or curing the acid-polymerisable or acid-curable material.

Upon exposure of the photopolymerisable composition to radiation of suitable wavelength, the photosensitiser is activated to yield a catalyst species capable of polymerising or curing the composition to yield a polymeric material, and according to a further aspect of the present invention there is provided a process for the preparation of a polymeric material which comprises subjecting a photopolymerisable composition as described in the immediately preceding paragraph to radiation of wavelength such as to activate the photosensitiser and polymerise or cure the composition.

The radiation may be ultra-violet or electron beam radiation, or may include wavelengths in the visible and the ultra-violet regions of the spectrum. The wavelength of the radiation suitably may be, for example, in the range from 200 mμ to 600 mμ. We prefer to employ radiation of wavelength in the range from 200 mμ to 400 mμ. Sunlight may be used as the radiation although the optimum wavelength of the radiation for any particular composition will depend upon the particular photosensitiser employed in that composition. The optimum wavelength in any particular case is easily determined by simple experiment, for example by determining the electronic absorption spectrum of the photosensitiser.

In the photosensitisers of formula I the groups R may be, for example, alkyl, cycloalkyl, aryl, alkaryl, or aralkyl groups or substituted derivatives thereof. Preferably each of the groups R is an aryl or substituted aryl group or one may be an alkyl group. Examples of substituents which may be present in the groups R are halogen, alkoxy, —COOR, —COR, —NO<sub>2</sub>, —NO, —OH and —SH.

In the case where one or more of the groups R in the photosensitiser is an alkyl or substituted alkyl group, it may contain from 1 to 20 carbon atoms, preferably from 2 to 6 carbon atoms. We prefer to employ salts wherein at least one, and preferably at least two, of the groups R is an aryl or alkaryl or substituted aryl or alkaryl group, especially the phenyl group or a group containing a phenyl group, for example —CH<sub>2</sub>CO Ph where Ph is the phenyl group. The preferred salts are sulphonium salts, i.e. salts of formula I wherein A is sulphur.

The anion X<sup>n-</sup> in the photosensitiser may be, for example, a halogen-containing complex ion selected from ClO<sub>4</sub><sup>-</sup> and metal halogenides. The metal halogenide may be, for example, a polyhalide or boron, antimony, tin, silicon, phosphorus, arsenic, bismuth or iron. Examples of suitable anions are tetrafluoroborate III (BF<sub>4</sub><sup>-</sup>), hexachloroantimonate V (S<sub>6</sub>Cl<sub>6</sub><sup>-</sup>), hexafluoroantimonate V (S<sub>6</sub>F<sub>6</sub><sup>-</sup>), hexachlorostannate IV (SnCl<sub>6</sub><sup>-</sup>), hexafluorophosphate (PF<sub>6</sub><sup>-</sup>), hexafluoroarsenate (AsF<sub>6</sub><sup>-</sup>), tetrachloroferrate III (FeCl<sub>4</sub><sup>-</sup>) and pentachlorobismuthate III (BiCl<sub>5</sub><sup>-</sup>).

Photosensitisers containing the anions described above, i.e. the perchlorate ion and metal halogenide ions, are suitable for polymerising or curing all types of acid-

polymerisable or acid-curable materials. The invention is not restricted, however, to use of photosensitisers containing these anions but includes use of photosensitisers which are capable of polymerising or curing some acid-polymerisable or acid-curable materials but not others. For example, salts (I) containing halide anions are capable of polymerising or curing urea/formaldehyde resins and melamine/formaldehyde resins but may not satisfactorily polymerise or cure epoxy resins and episulphide resins. The ability of a particular salt to polymerise or cure a material depends upon the nucleophilicity of its anion; salts containing strongly nucleophilic anions which readily form covalent bonds with carbon atoms to yield stable compounds, for example halide ions, in general will polymerise or cure urea/formaldehyde and melamine/formaldehyde resins but may not polymerise or cure epoxy resins and episulphide resins. Examples of other anions of this type are  $\text{CF}_3\text{COO}^-$ ,  $\text{SO}_3\text{F}^-$ ,  $\text{ArSO}_3^-$  (where Ar is an aromatic group, e.g. the toluyl group),  $\text{NO}_3^-$  and the picrate ion. We do not exclude the possibility that some of these anions will provide photosensitisers which will also cure epoxy resins. The ability of a particular photosensitiser to cure the particular material depends upon the ability of the corresponding proton acid, i.e. the proton acid containing the same anion as the photosensitiser, to cure that material. In general if the acid polymerises or cures the material, then the corresponding salt containing the same anion also will be capable of polymerising or curing the material. Thus the suitability of a particular salt for use with a particular acid-polymerisable or acid-curable material generally is readily determined simply by mixing the corresponding proton acid with the material.

It is believed that the photosensitiser releases acid upon exposure to suitable radiation, for example ultraviolet light. The preferred anions for polymerising or curing epoxy and episulphide materials, on account of the rapid rate of polymerisation or curing which is induced, are  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$  and  $\text{SbF}_6^-$ .

The photosensitisers used in this invention are normally solids at ordinary temperatures and they are usually incorporated in the acid-polymerisable or acid-curable material in the form of a solution in an inert liquid diluent, that is a liquid diluent which is chemically inert towards the ingredients of the composition. Any inert liquid diluent in which the photosensitiser is sufficiently soluble may be used, and examples of suitable diluents are halogenated hydrocarbons, e.g. methylene chloride, ketones, e.g. acetone, and alcohols, e.g. ethanol. We prefer to employ a liquid diluent of low boiling point, e.g. below  $150^\circ\text{C}$ , in order to facilitate removal of the diluent from the composition. The amount of the diluent used is not critical but preferably is just sufficient to dissolve the appropriate amount of the photosensitiser. After incorporation of the photosensitiser in the composition, the diluent may be removed, if desired, before the composition is irradiated. Removal of the diluent prior to irradiating the composition may be desirable in cases where the diluent is a solvent for the acid-polymerisable or acid-curable material. In the case where the material is, or contains, a monomer, the photosensitiser may be soluble in the material and a diluent may not be required.

The amount of the photosensitiser is not critical but will usually be from 0.01% to 10.0%, and preferably from 0.5% to 5.0% by weight based on the weight of acid-polymerisable and/or acid-curable material in the composition. In general increasing the amount of the photosensitiser results in an increase in the rate of polymerisation or curing achieved although in practice there is little point in using an amount of greater than 10% by weight. The photosensitiser preferably should be soluble in the resin into which it is incorporated and the solubility of a particular photosensitiser in the resin may limit the amount of that salt which can be incorporated. The polymerisation or curing reaction initiated by irradiating the composition is exothermic and use of too large an amount of the photosensitiser may result in a very rapid rise in temperature and loss of control over the reaction conditions. The optimum amount of the photosensitiser will usually be about 3% to 5% by weight but will depend upon the particular salt and acid-polymerisable or acid-curable material employed and the radiation source, and can be determined by simple experiment.

In general, polymerisation or curing of the composition proceeds readily when the composition is irradiated at ambient temperature although the reaction is exothermic and may be accompanied by a rise in temperature of the composition. The rate of polymerisation or curing in general is increased by irradiating the composition at an elevated temperature.

Any acid-polymerisable or acid-curable material may be employed in the present invention. Mixtures of acid-polymerisable and/or acid-curable materials may be employed, as also may mixtures of one or more acid-polymerisable or acid-curable materials and resins which are not acid-curable, for example alkyd resins. Materials

containing acid-polymerisable cyclic groups may be employed, notably cyclic ethers for example lactones and acrolein tetramer and especially epoxides and episulphides, and polymers thereof containing polymerisable cyclic groups. Epoxides and episulphides containing from 2 to 20 carbon atoms are suitable, for example ethylene oxide, ethylene sulphide, propylene oxide and propylene sulphide, as also are compounds containing two or more epoxide or episulphide groups. Epoxy and episulphide resins may be used, for example the epoxy resins commonly known as 'Araldite' epoxy resins. Other acid-curable resins which may be used include phenolic resins, for example phenol/formaldehyde resins, aminoplastics for example urea/formaldehyde and melamine/formaldehyde resins, methylol compounds, methylol ethers of polycarboxylic acid amides, for example derivatives of polyacrylic and polymethacrylic acid amides, alkyd resins containing urethane groups and resins containing carbonic acid esters of N-methylolamides. Acid-polymerisable or acid-curable ethylenically unsaturated materials may also be used, for example styrene, vinyl carbazole, vinyl ethers and diketene (which is both ethylenically unsaturated and a lactone). Resinous materials containing cross-linking agents which can be cured by acids are included.

The compositions of the invention may be used in any of the applications for which acid-curable resin compositions are normally employed, provided that, if the composition is to be polymerised or cured *in situ*, irradiation of the composition is possible. Thus the compositions may be used, for example, for forming surface coatings on a variety of substrates, e.g. wood, paper, metals and textiles, and in printing inks. They may be used as adhesives in applications where they can be subjected *in situ* to radiation, for example in the formation of laminates wherein one or both of the lamina is permeable to radiation, e.g. glass lamina and some plastics lamina. The compositions have the property that only those regions contacted by radiation are polymerised or cured so that they may be used for example in the production of decorative articles having a contoured surface by exposing parts of the surface to radiation to cure those parts and subsequently removing uncured material from the surface. Thus they may be used, for example in the production of printing plates and printed circuits. The compositions of the invention may contain foaming agents and they may be foamed prior to irradiating them so that subsequently irradiating them cures or sets the foam.

When a resin composition according to the invention is irradiated, polymerisation or curing commences at the exposed surface and spreads inwardly. The depth of cure achieved is limited by the depth of penetration of the composition by the radiation. This property can be utilised in the production of skinned materials such as skinned foams. Thus for example a foamable resin composition may be irradiated prior to foaming to form a thin surface layer of cured material which is non-foamable and the remainder of the composition may then be foamed to yield a foam having an integral skin. One or more surface of the composition may be skinned in this way. Foams having contoured skinned surfaces may be produced.

The compositions of the invention may contain inert fillers and pigments provided these do not prevent penetration of the composition by the radiation used to activate the sulphonium salt. If desired, the composition may contain one or more additional photosensitisers, for example to render the composition activatable by radiation which would not activate the sulphonium salt in the absence of the additional photosensitiser.

The invention is illustrated but in no way limited by the following examples.

#### Example 1.

0.3 g of diphenyl ethyl sulphonium tetrafluoroborate was dissolved in a few ml of acetone and the solution was mixed into 9.7 g of an epoxy resin available as Araldite MY753 epoxy resin from Ciba-Geigy. The mixture was painted on a steel plate and left to stand for 10 minutes to allow the acetone to evaporate and then the coated plate was exposed to radiation from two 2 kw 'Philips' HTQ7 lamp tubes (known as the HTQ light printing-lamp) placed at a distance of 8 inches from the plate. The spectral energy output of the lamp, expressed as wavelength in mμ (energy %) was 248 (1.7), 254—8 (3.5), 265 (3.7), 270 (0.7), 275 (0.7), 280 (1.7), 289 (1.0), 297 (3.0), 302 (4.7), 313 (12.1), 334 (1.4), 366 (20.6), 405 (6.1), 436 (12.4), 492 (0.7), 546 (11.2), 578 (14.8). After two minutes the plate was removed and was found to be coated with a hard (pencil hardness >4H), solvent-resistant film. Solvent resistance was determined by rubbing the film with tissue soaked in acetone 20 times and noting the visible effect, if any, produced by this treatment.

A further mixture as above was prepared and stored in a dark bottle in a dark cupboard at ambient temperature. After 3 months the composition exhibited no

noticeable signs of gelation and was curable by irradiation as if it had been freshly prepared.

#### Example 2.

The procedure of Example 1 was repeated using 0.3 g of triphenyl sulphonium tetrafluoroborate and 9.7 g of an epoxy resin available as 'Araldite' CT200 epoxy resin from Ciba-Geigy. The resin was a solid, and was employed as a solution in a 1:1 mixture of acetone and xylene. After 2 minutes irradiation, a hard (pencil hardness 5H), solvent resistant coating was produced.

#### Example 3.

The procedure of Example 1 was repeated using 0.3 of diphenyl ethyl sulphonium tetrafluoroborate and 9.7 of an epoxy resin available as 'Araldite' MY750 epoxy resin. After 2 minutes irradiation, a hard, solvent-resistant film had been produced.

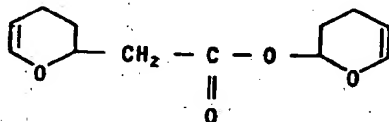
#### Example 4.

The procedure of Example 2 was repeated using 0.3 g of diphenyl ethyl sulphonium tetrafluoroborate instead of the triphenyl sulphonium tetrafluoroborate. A hard (5H), solvent resistant film was obtained after 2 minutes irradiation.

In a further experiment the above procedure was repeated except that the coated plate was irradiated image-wise through holes in a sheet of aluminium foil out of which a variety of shapes had been cut. After 1½ minutes irradiation, the coated plate was washed with cold acetone which resulted in removal of composition which had not been irradiated, leaving raised areas of a hard film in shapes corresponding to the shapes of the holes in the aluminium foil through which the coated plate has been irradiated.

#### Example 5.

A liquid mixture of 0.3 g of diphenyl ethyl sulphonium tetrafluoroborate and 9.7 g of acrolein tetramer



was painted onto a steel plate and the coated plate was irradiated as is described in Example 1. After 3 minutes irradiation the plate was removed and the coating had set into a hard (5H), solid film which was not fully resistant to acetone.

#### Example 6.

The procedure of Example 2 was repeated except that the amount of the triphenyl sulphonium tetrafluoroborate was increased to 5% by weight of the composition and irradiation was 30 seconds instead of 2 minutes. A solvent-resistant film of pencil hardness 6H was obtained.

#### Example 7.

The procedure of Example 1 was repeated but using 'Araldite' CT179 epoxy resin instead of 'Araldite' MY753 resin and using triphenyl sulphonium tetrafluoroborate. A solvent-resistant film of pencil hardness 6H was obtained.

In a further experiment the amount of the triphenyl sulphonium tetrafluoroborate was increased to 5% by weight and irradiation was for 30 seconds instead of 2 minutes. A solvent-resistant film of pencil hardness 6H was obtained.

#### Example 8.

0.3 g of triphenyl sulphonium tetrafluoroborate was dissolved in a few ml of acetone and the solution was mixed into 9.7 g of a urea/formaldehyde resin-alkyd resin mixture comprising a mixture of 2 parts of butylated urea/formaldehyde and 3 parts of tall oil alkyd in a mixture of solvents (solids content 44% by weight). The mixture was painted onto a steel plate and allowed to stand for 10 minutes to allow the solvent to evaporate and then the painted plate was irradiated as described in Example 1 for 1 minute. A solvent-resistant film of pencil hardness 6H was obtained.

## Example 9.

The procedure of Example 8 was repeated but using diphenyl ethyl sulphonium tetrafluoroborate, and irradiation was for 2 minutes. A solvent-resistant film of pencil hardness 6H was obtained.

## Example 10.

The procedure of Example 8 was repeated using triphenyl sulphonium hexachloroantimonate instead of the tetrafluoroborate. After 1 minute of irradiation, a solvent-resistant film of pencil hardness 6H had been obtained.

## Example 11.

The procedure of Example 5 was repeated using 0.3 g of triphenyl sulphonium chloride instead of the diphenyl ethyl sulphonium tetrafluoroborate. After irradiation for 3 minutes, the sample was found to be a solvent-resistant film of a pencil hardness 6H.

## Example 12.

A variety of sulphonium salts were employed to cure 'Araldite' CY179 epoxy resin using the procedure described in Example 1. The sulphonium salt employed, its concentration by weight based on the epoxy resin and the time for which the sample was irradiated are shown in the Table below. In each experiment, a hard (pencil hardness >4H), solvent-resistant film was obtained.

TABLE

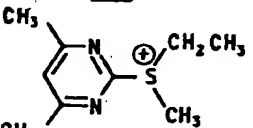
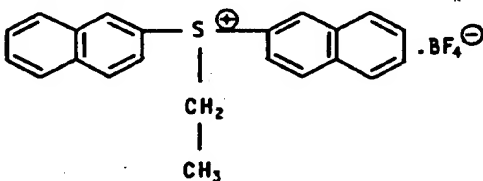
Sulphonium Salt	Concn. (% w/w)	Exposure Time (seconds)
$\text{Ph}_3\text{S}^{\oplus}.\text{PF}_6^{\ominus}$	2	20
$\text{Ph}_3\text{S}^{\oplus}.\text{PF}_6^{\ominus}$	4	10 *
$(\text{CH}_3)_3\text{S}^{\oplus}.\text{BF}_4^{\ominus}$	2	210
$(\text{CH}_3)_3\text{S}^{\oplus}.\text{BF}_4^{\ominus}$	4	210
$(\text{HO CH}_2\text{CH}_2)_3\text{S}^{\oplus}.\text{BF}_4^{\ominus}$	2	270
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CO CH}_2\text{S}^{\oplus}(\text{CH}_2\text{CH}_2\text{OH})_2.\text{BF}_4^{\ominus}$	2	120
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CO CH}_2\text{S}^{\oplus}(\text{CH}_2\text{CH}_2\text{OH})_2.\text{BF}_4^{\ominus}$	4	120
 $\text{BF}_4^{\ominus}$	4	180
$(\text{Ph}_3\text{S}^{\oplus})_2.\text{SnCl}_6^{2-}$	2	240
 $\text{BF}_4^{\ominus}$	3	120

TABLE (Continued)

Sulphonium Salt	Concn. (% w/w)	Exposure Time (seconds)
	2	120
	2	105
	4	60
	2	30
	4	20
	6	20
	2	25
	4	5
	2	25
	4	10
	4	10

TABLE (Continued)

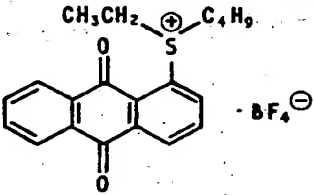
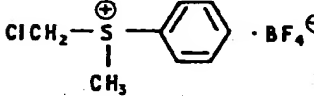
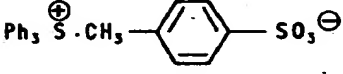
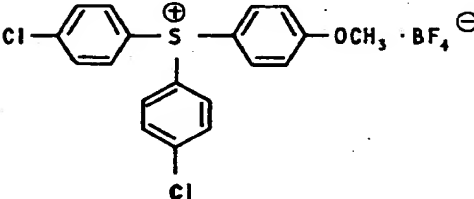
Sulphonium Salt	Concn. (% w/w)	Exposure Time (seconds)
	4	90
$(\text{CH}_3)_2\text{S}^+-\text{CH}_2\text{C}\equiv\text{CH} \cdot \text{BF}_4^-$	2	150
	4	150
$(\text{CH}_3)_2\text{S}^+-\text{COOCH}_2\text{CH}_3 \cdot \text{BF}_4^-$	2	150
	4	130
	2	90
	4	90
$\text{Ph}_3\text{S}^+ \cdot \text{CF}_3\text{COO}^-$	4	180
$\text{Ph}_3\text{S}^+ \cdot \text{NO}_3^-$	4	240
$\text{Ph}_3\text{S}^+ \cdot \text{SbF}_6^-$	2	10
	4	10*
$\text{Ph}_3\text{S}^+ \cdot \text{AsF}_6^-$	2	15
	4	10
$\text{Ph}_3\text{S}^+ \cdot \text{I}^-$	2	150
	4	150
	2	150
	4	150
	4	25



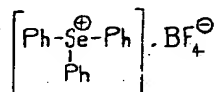
TABLE (Continued)

Sulphonium Salt	Concn. (% w/w)	Exposure Time (seconds)
$\text{CH}_3-\text{S}^+-\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH}) \text{PF}_6^-$	2	25
$\text{CH}_3-\text{S}^+-\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH}) \text{PF}_6^-$	4	20*
$\text{CH}_3-\text{S}^+-\text{C}_6\text{H}_4(\text{OH}) \text{PF}_6^-$	4	20
$\text{Ph}_3\text{S}^+ \cdot \text{FeCl}_4^-$	4	180
$\text{C}_6\text{H}_{11}\text{S}^+-\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH}) \cdot \text{BF}_4^-$	2	25
$\text{C}_6\text{H}_{11}\text{S}^+-\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH}) \cdot \text{BF}_4^-$	4	25
$\text{C}_6\text{H}_{11}\text{S}^+-\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH}) \text{Br}^-$	2	120
$\text{C}_6\text{H}_{11}\text{S}^+-\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH}) \text{Br}^-$	4	120

\* In these experiments a tack-free film was obtained after 2 to 3 seconds.

## Example 13.

0.3 g of triphenyl selenium tetrafluoroborate



5 is dissolved in a few ml of acetone and the solution is mixed into 9.7 g of an epoxy resin available as Araldite CY179 epoxy resin from Ciba-Geigy. The mixture is painted on a steel plate and left to stand for 10 minutes to allow the acetone to evaporate and then the coated plate is exposed to radiation from two 2 kw 'Philips' HTQ7 lamp tubes (known as the HTQ light printing lamp) placed at a distance of 8 inches from the plate. The spectral energy output of the lamp, expressed as wavelength in mμ (energy %) was 248 (1.7), 254—8 (3.5), 265 (3.7), 270 (0.7), 275 (0.7), 280 (1.7), 289 (1.0), 2.97 (3.0), 302 (4.7), 313 (12.1), 334 (1.4), 366 (20.6), 405 (6.1), 436 (12.4), 492 (0.7), 546 (11.2), 578 (14.8). After two minutes the plate is removed and found to be coated with a solvent-resistant film of pencil hardness >4H. Solvent resistance is determined by rubbing the film with tissue soaked in acetone 20 times and noting the visible effect, if any, produced by this treatment. 10 15

## Example 14.

20 The procedure described in Example 1 was employed to cure the resins identified below by their trade names, using as photosensitizer triphenyl sulphonium hexafluorophosphate in an amount of 4%, by weight based on the resin (0.08 g of photosensitizer dissolved in 0.5 g acetone and mixed with 2 g of the resin). In each experiment a hard, solvent resistant film was obtained. 20


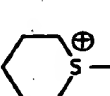
	Resin	Exposure Time Seconds	
	'Epikote' 816 (Shell)	20	
	'Epikote' 828 (Shell)	15	
5	'Araldite' LY558 (Ciba)	15	5
	'Araldite' CT200 (50% w/w solution in a 1:1 acetone:xylene mixture)	25	
	'Araldite' MY 753	30	
10	Urea/formaldehyde resin (as in Example 8)	90	10
	'Cibamin' ML 1000 GB (a methylated melamine- formaldehyde resin)	105	

## Example 15.

The procedure described in Example 1 was repeated using the epoxy resins, photosensitisers and exposure times listed below. In each experiment a hard, acetone-resistant film was produced.

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Resin (2g)	Photosensitiser (in 0.5 ml acetone)	Concn. (g)	Exposure Time (seconds)
'Araldite' LY 558	dimethyl-( <i>p</i> -hydroxy- <i>m</i> -tolyl) sulphonium hexafluorophosphate	0.08 0.04	30 30
'Epikote' 828	"	0.08	30
'Epikote' 828		0.08	25
'Araldite' LY 558	 . PF <sub>6</sub> <sup>⊖</sup>	0.08	30
'Araldite' CT 200		0.08	45
'Epikote' 828	 . BF <sub>4</sub> <sup>⊖</sup>	0.08	45

## Example 16.

The procedure described in Example 1 was repeated except that the epoxy resin was Araldite GY 250 epoxy resin. The exposure time was 60 seconds after which time a hard, solvent-resistant film had been produced.

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## Example 17.

A solution of triphenyl sulphonium tetrafluoroborate (0.008 g) in methylene chloride (3 g) and 2.2 g of isobutyl vinyl ether was irradiated in a glass vial placed at the centre of 8 x 20 w 'Philips' "black-light" fluorescent tubes circularly disposed (diameter=8 inches) and surrounded by a cylindrical reflector made of a polished metal sheet.

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After about 30 seconds exothermic reaction resulted, demonstrated by boiling of the mixture. The colour of the mixture gradually changed to yellow and then red and a greenish fluorescence was observed. After about 2 minutes a rather viscous mass resulted caused by polymerisation of the vinyl ether.

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## Example 18.

A solution of triphenyl sulphonium tetrafluoroborate (0.02 g) and N-vinyl carbazole (2.5 g) in methylene chloride (3.5 ml) was irradiated as in Example 17.

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After about 25 seconds exothermic reaction resulted accompanied by a colour change and fluorescence, and the solution became rather viscous after 2 minutes as a result of polymerisation of the N-vinyl carbazole.

## Example 19.

The procedure of Example 17 was repeated using 0.02 g triphenyl sulphonium tetrafluoroborate in 2 ml of propylene sulphide. After 10 minutes of irradiation the solution became warm and after a further 5 minutes a solid clear mass had been produced.

## Example 20.

A mixture was prepared as described in Example 1 and stored in a dark bottle in a dark cupboard at ambient temperature. After 12 months the composition exhibited no noticeable signs of gelation and was curable by irradiation as if it had been freshly prepared.

Compositions prepared as described in Example 1 but using the following epoxy resins were stored as above for a period of 12 months.

'Araldite' MY 750

'Araldite' CT 200

'Araldite' CY 250

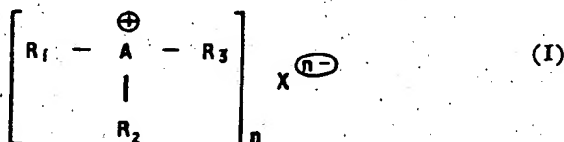
'Cibamin' ML 1000 GB

In each experiment the composition showed no noticeable signs of gelation and was curable by irradiation as if it had been freshly prepared.

The words 'Araldite', 'Philips', 'Epikote' and 'Cibamin' are Registered Trade Marks.

## WHAT WE CLAIM IS:—

1. A photopolymerisable composition comprising at least one acid-polymerisable or acid-curable material and as photosensitiser at least one salt of formula



wherein A is sulphur, selenium or tellurium, n is 1 or 2, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, which may be the same or different, each is a hydrocarbon or substituted hydrocarbon group or heterocyclic group or two of the groups R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> together with the element A are a heterocyclic structure the other group R being a hydrocarbon or a substituted hydrocarbon group, and X<sup>⊖</sup> is an anion derived from an acid which is capable of polymerising or curing the acid-polymerisable or acid-curable material.

2. A photopolymerisable composition as claimed in claim 1 wherein in the photosensitiser the element A is sulphur.

3. A photopolymerisable composition as claimed in claim 1 or 2 wherein the amount of the photosensitiser is from 0.01% to 10% by weight based on the weight of the acid-polymerisable or acid-curable material.

4. A photopolymerisable composition as claimed in claim 3 wherein the amount of the photosensitiser is from 0.05% to 5% by weight based on the weight of the acid-polymerisable or acid-curable material.

5. A photopolymerisable composition as claimed in claim 4 wherein the amount of the photosensitiser is from 3% to 5% by weight based on the weight of the acid-polymerisable or acid-curable material.

6. A photopolymerisable composition as claimed in any one of the preceding claims wherein the anion X<sup>⊖</sup> is a halogen-containing complex ion selected from ClO<sub>4</sub><sup>⊖</sup> and metal halogenides.

7. A photopolymerisable composition as claimed in claim 6 wherein the anion X<sup>⊖</sup> is a polyhalide of boron, antimony, tin, silicon, phosphorus, arsenic, bismuth or iron.

8. A photopolymerisable composition as claimed in claim 7 wherein the anion X<sup>⊖</sup> is the tetrafluoroborate ion.

9. A photopolymerisable composition as claimed in any one of the preceding claims wherein the photosensitiser is soluble in the acid-polymerisable or acid-curable material.

10. A photopolymerisable composition as claimed in any one of the preceding claims wherein in the photosensitiser at least one of the groups R is an aryl group or substituted aryl group.

11. A photopolymerisable composition as claimed in claim 10 wherein in the photosensitiser each of the groups R is an aryl group or substituted aryl group.

12. A photopolymerisable composition as claimed in claim 10 wherein two of the groups R are aryl groups or substituted aryl groups, the other group R being an alkyl group.

13. A photopolymerisable composition as claimed in claim 10, 11 or 12 wherein the photosensitiser contains at least one phenyl group.

14. A photopolymerisable composition as claimed in any one of the preceding claims wherein the acid-curable material comprises an epoxy resin.

15. A photopolymerisable composition as claimed in any one of claims 1 to 13 wherein the acid-polymerisable material is an acid-polymerisable monomer.

16. A photopolymerisable composition substantially as described herein with particular reference to any one of Examples 1 to 11.

17. A photopolymerisable composition substantially as described herein with particular reference to Example 12.

18. A photopolymerisable composition as described herein with particular reference to Example 13.

19. A polymeric composition derived from a photopolymerisable composition as claimed in any one of claims 1 to 18 by subjecting the photopolymerisable composition to radiation of wavelength such as to activate the photosensitiser and polymerise or cure the composition.

20. A polymeric composition as claimed in claim 19 which is in the form of a surface coating on a substrate.

21. A process for the preparation of a polymeric composition which comprises subjecting a photopolymerisable composition as claimed in any one of claims 1 to 18 to radiation of wavelength such as to activate the photosensitiser and polymerise or cure the composition.

22. A process as claimed in claim 21 wherein the radiation comprises ultra-violet radiation.

23. A process as claimed in claim 21 or 22 wherein the wavelength of the radiation is in the range from 200 microns to 600 microns.

24. A process as claimed in claim 21 substantially as described herein with particular reference to the Examples.

25. A polymeric composition as claimed in claim 20 substantially as described herein with particular reference to the Examples.

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